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FLEXIBLY BRIDGED BINUCLEAR RHODIUM AND IRIIDIUM
COMPLEXES OF P-XYLENEBIS(3,4,5,6-TETRAFLUOROPHENYL) (U) ROCHESTER UNIV NY DEPT
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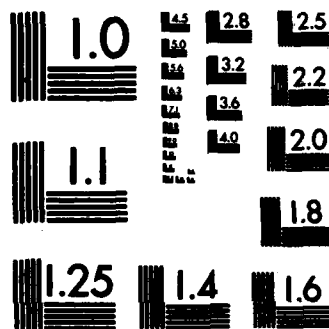
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Flexibly Bridged Binuclear Rhodium and Iridium
Complexes of p-Xylylenebis(3-(2,4-pentanedione))

by

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15. ABSTRACT (Continue on reverse side if necessary and identify by block number) Binuclear complexes of Rh and Ir containing a flexibly bridging bis(acac) ligand have been synthesized and characterized. The reaction of $[\text{M}(\mu\text{-Cl})(1,4\text{-C}_6\text{H}_4)_2]_2$ (M=Rh, Ir) with p-xylylenbis(3-(2,4-pentanedione)), $\text{xy}(\text{acac})_2$, + 2 equiv KOH results in the formation of the binuclear compounds $[\text{M}(\text{CO})_2\text{xy}(\text{acac})_2]$. The cyclooctadiene ligand in these complexes is readily displaced from the metal centers by either CO or PPh_3 leading to the formation of $[\text{M}(\text{CO})_2\text{xy}(\text{acac})_2]$ and $[\text{M}(\text{PPh}_3)_2\text{xy}(\text{acac})_2]$, respectively. The $[\text{M}(\text{CO})_2\text{xy}(\text{acac})_2]$ complexes react with excess triphenylphosphine, leading to $[\text{M}(\text{CO})_2\text{xy}(\text{acac})_2\text{P}(\text{Ph})_3]$.			

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displacement of one CO from each metal center and the formation of $[\text{M}(\text{CO})(\text{PPh}_3)]_2\text{xy}(\text{acac})_2$. The rhodium complex $[\text{Rh}(\text{CO})_2\text{xy}(\text{acac})_2]$ also reacts with triphenylphosphite to produce the phosphite derivative, $[\text{Rh}(\text{P}(\text{OPh})_3)_2\text{xy}(\text{acac})_2]$, which is found to act as a catalyst precursor for propylene hydrogeneration. At 24°C and under 320 torr of H_2 + C_3H_6 (2.5:1), propene forms at the rate of 8 mol product mol⁻¹ catalyst h⁻¹ in the presence of a 7.4500-M solution of the phosphite derivative in toluene. The binuclear iridium complex $[\text{Ir}(\text{CO})(\text{PPh}_3)]_2\text{xy}(\text{acac})_2$ undergoes oxidative addition reactions with allyl bromide or benzyliodide producing the iridium(III) species $[\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{xy}(\text{acac})_2]$ where R = o-allyl and benzyl, respectively. The mononuclear iridium complex $[\text{Ir}(\text{PPh}_3)_2\text{xy}(\text{acac})_2]$ has also been synthesized and characterized. The reaction of this complex with H_2 results in the formation of $[\text{IrH}_2(\text{PPh}_3)_2\text{xy}(\text{acac})_2]$, whereas the reaction of $[\text{Ir}(\text{CO})(\text{acac})_2]$ with H_2 in the presence of 2 equiv of PPh_3 leads to the formation of H_2 - and $\text{Ir}(\text{CO})\text{Ir}(\text{PPh}_3)_2$ as determined by IR and spectroscopy. The significance of these reactions in terms of the stability of rhodium and iridium acac complexes in catalytic systems is discussed.

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Flexibly Bridged Binuclear Rhodium and Iridium

Complexes of μ -Xylylenabis(3-(2,4-pentanedione))

Bryan C. Whitmore and Richard Eisenberg

ABSTRACT

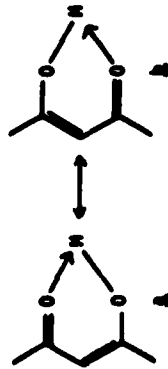
Binuclear complexes of Rh and Ir containing a flexibly bridging bis(acac) ligand have been synthesized and characterized. The reaction of $[M(\eta^5\text{-C}_5\text{H}_5)(1,5\text{-C}_5\text{H}_7\text{O}_2)_2]^-$ ($M = \text{Rh}, \text{Ir}$) with μ -xylylenabis(3-(2,4-pentanedione)), $\text{xy}(\text{Hacac})_2$, + 2 equiv KOH results in the formation of the binuclear compounds $(M(\text{CO}))_2\text{xy}(\text{acac})_2$. The cyclooctadiene ligand in these complexes is readily displaced from the metal centers by either CO or PPh_3 leading to the formation of $(M(\text{CO}))_2\text{xy}(\text{acac})_2$ and $(M(\text{PPh}_3)_2)_2\text{xy}(\text{acac})_2$, respectively. The $(M(\text{CO}))_2\text{xy}(\text{acac})_2$ complexes react with excess triphenylphosphine, leading to the displacement of one CO from each metal center and the formation of $(M(\text{CO}))(PPh_3)_2\text{xy}(\text{acac})_2$. The Rhodium complex $(\text{Rh}(\text{CO}))_2\text{xy}(\text{acac})_2$ also reacts with triphenylphosphite to produce the phosphite derivative, $(\text{Rh}(\text{P(OPh)}_3)_2)_2\text{xy}(\text{acac})_2$, which is found to act as a catalyst precursor for propylene hydrogenation. At 24°C and under 320 torr of H_2 + C_3H_6 (2.5:1), propane forms at the rate of 8 mol product mol^{-1} catalyst h^{-1} in the presence of a $7.4 \times 10^{-4} \text{M}$ solution of the phosphite derivative in toluene. The binuclear iridium complex $(\text{Ir}(\text{CO}))_2(\text{PPh}_3)_2\text{xy}(\text{acac})_2$ undergoes oxidative addition reactions with allyl bromide or benzyl bromide producing the iridium(III) species $(\text{Ir}(\text{R}(\text{CO})(\text{PPh}_3)_2)_2\text{xy}(\text{acac})_2$ where R = α -allyl and benzyl, respectively. The mononuclear iridium complex $\text{Ir}(\text{PPh}_3)_2(\text{acac})$ has also been synthesized and characterized. The reaction of

this complex with H_2 results in the formation of $\text{IrH}_2(\text{PPh}_3)_2(\text{acac})$, whereas the reaction of $\text{Ir}(\text{CO})(\text{acac})$ with H_2 in the presence of 2 equiv of PPh_3 leads to the formation of mer- and $\text{fac-IrH}_3(\text{PPh}_3)_3$ as determined by ^1H NMR spectroscopy. The significance of these reactions in terms of the stability of rhodium and iridium acac complexes in catalytic systems is discussed.

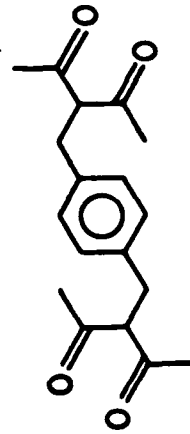
Introduction

Transition metal complexes of β -diketonate ligands have been studied for many years because of the number and variety of stable complexes which they form, and the spectroscopic and chemical properties which these complexes exhibit.^{1,2}

In these complexes, the 6-membered chelate ring possesses a delocalized electronic structure, as suggested by resonance forms **A** and **B**, and exhibits partial aromatic character as evidenced by reaction chemistry of the acetylacetonate (acac) chelate ring.³



We describe in the present study the preparation of binuclear complexes based on a ligand system which contains two acac moieties. The β -diketonate groups of the ligand system are connected by a xylylene bridge and are precluded from binding to a single metal center. The ligand, *p*-xylylenobis[3-(2,4-pentanedione)] (*xyl*(*hacac*)₂), shown as **1**, was first prepared in 1959,⁴ and was studied briefly as

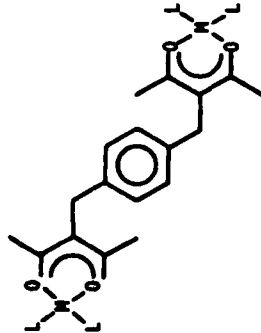


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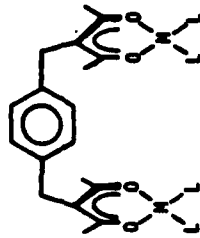
a component in the formation of both organic⁵ and coordination⁶ polymers. We envisioned that this bis(acac) compound would act as a flexible bridging ligand in the preparation of binuclear rhodium and iridium complexes, the mononuclear analogues of which have been studied extensively. Since 1964, when the rhodium complex $\text{Rh}(\text{CO})_2(\text{acac})$ and closely related derivatives were first reported,⁷ many

rhodium and iridium acac complexes have been studied and described in the literature. Some of the Rh systems have found use as catalyst precursors for hydrogenation⁸ and hydroformylation⁹ reactions.

The Rh and Ir binuclear complexes based on **1** belong to a group of flexibly-bridged binuclear systems which, according to molecular models, possess metal centers separated by distances that vary from a minimum of 4 Å to a maximum of 12 Å. The flexibility of the binuclear systems results from rotational freedom about the C(phenyl)-C(phenyl) bond of the xylylene unit. The conformation presumed to be most stable sterically has a trans arrangement of the complexed metal ions, as shown by **II**. However, the flexibility of the *xyl*(acac)₂ ligand allows a facile face-to-



II



III

face approach of the transition metal centers, **III**, thereby providing a site for substrate binding between the metal ions in an intramolecular fashion. Complexes of this type thus have the potential to serve as multi-electron binuclear catalysts.

Experimental Section

All reactions were routinely performed under an N_2 atmosphere using either modified Schlenk techniques or a Vacuum Atmospheres dry box. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Physical Measurements. 1H and ^{31}P NMR spectra were recorded on a Bruker WM400 400-MHz instrument with chemical shifts reported in ppm relative to Me_4Si . Deuterated solvents were purchased from Aldrich, dried over sodium and distilled in $vacuo$ prior to use. Infrared spectra were recorded on a Perkin-Elmer Model 467 grating spectrophotometer. Samples were either KBr pellets or mujol mulls on NaCl plates. Electronic spectra were recorded on a Perkin-Elmer Model 330 spectrophotometer. Extinction coefficients are given in $M^{-1}cm^{-1}$. Mass spectra were recorded on a Dupont 490-B GC-MS mass spectrometer.

Reagents. All solvents used were analytical reagent grade except where otherwise noted. THF was distilled from sodium-lead alloy and benzophenone under N_2 prior to use. $[Rh(u-CI)(1,5-COO)]_2^{10}$, $[Ir(u-CI)(1,5-COO)]_2^{11}$ and p -xylylenebis-(3-(2,4-pentanedione))⁶ were prepared by literature methods.

$[p\text{-xylylenebis(3-(2,4-pentanedionato))bis(rhodium(cyclooctadiene))](2)$

$Rh_2(COO)_2(u-CI)_2$ (0.50g, 1 mmol) and p -xylylenebis(3-(2,4-pentanedione))(0.30g, 1 mmol) are combined in degassed diethyl ether (10 mL) under a nitrogen atmosphere at $-78^\circ C$. Aqueous KOH (2mL, 1M) is then added dropwise over 10 min. The resulting solution is stirred under nitrogen at $0^\circ C$ for 45 minutes. Ether (5 mL) and water (10 mL) are then added to the reaction solution, the organic layer is separated and the aqueous phase extracted with 1:1 THF/diethylether (4 x 25 mL). The combined organic phase is then dried over $MgSO_4$, filtered, reduced in volume to 10 mL, and chilled. The resulting yellow ppt. is filtered and washed with ethanol. The filtrate volume is reduced by 50%, yielding additional product by precipitation. Combined yield, 0.50g (69%) Anal. Calcd for $C_{34}H_{40}O_8Rh_2$: C, 56.52; H, 6.14. Found: C, 56.51; H, 6.39. IR (KBr): 1554, 1430, 1354, 1272, 1019, 950, 455 cm^{-1} .

Mass spectrum (m/e): 722 (M^+), 679, 512, 470, 469 (Base). 1H NMR ($CDCl_3$): 7.03 (s, 4, aromatic), 4.05 (s, 8, vinyl), 3.60 (s, 4, benzylic), 2.41, 1.85 (multiplets, 16, methylene), 1.96 (s, 12, methyl).

$[p\text{-xylylenebis(3-(2,4-pentanedionato))bis(rhodium di(carboxyl))](2)$

Carbon monoxide is passed through a stirred suspension of 1 (0.50g, 0.69 mmol) in hexane (10 mL) for 30 min. The orange precipitate, 2, is filtered, washed with hexanes (10 mL), diethyl ether (15 mL) and dried in vacuo. Yield, 0.35g (81%). Anal. Calcd for $C_{22}H_{20}O_8Rh_2$: C, 42.74; H, 3.26; N, 3.26: 0.20.70. Found: C, 42.60; H, 3.43; 0.20.48. IR (KBr): 2070, 1970, 1563, 1450, 1370, 1289, 1172, 1023, 954, 527, 467. 1H NMR (CD_2Cl_2): 7.01 (s, 4, aromatic), 3.70 (s, 4, benzylic), 2.09 (s, 12, methyl).

[p-Xyl]enebis(3-(2,4-pentanedionato))bis(rhodium(carbonyl)(triphenylphosphine)) (1).

Triphenylphosphine (0.065g, 0.32 mmol) is added to **2** (0.10g, 0.16 mmol) in THF (5 mL) under N_2 . The solution is stirred for 30 min and the solvent removed in vacuo. The solid residue is washed with diethyl ether (20 mL) and dried in vacuo. Yield, 0.17g (98%). Anal. Calcd for $C_{54}H_{50}P_2O_6Rh_2$: C, 61.02; H, 4.75; P, 5.83; O, 9.03. Found: C, 61.20; H, 4.66; P, 5.90; O, 8.84. IR(KBr): 1964, 1560, 1435, 1362, 1204, 1100, 951, 751, 606, 597, 531, 462. 1H NMR (CD_2Cl_2): 7.35-7.80 (m, 30, aromatic); 7.00 (s, 4, aromatic); 3.62 (s, 4, benzyl); 2.10 (s, 6, methyl); 1.62 (s, 6, methyl).

[p-Xyl]enebis(3-(2,4-pentanedionato))bis(rhodium bis(triphenylphosphite)) (4).

To a suspension of **2** (0.021 g, 0.035mmol) in degassed diethyl ether (5 mL) under N_2 is added triphenylphosphite (46mL, 0.175mmol). The solution rapidly clears followed by formation of yellow needles. The yellow solid is filtered in air, washed with diethyl ether (10 mL) and dried in vacuo. Yield, 0.066 g (92%). Anal. Calcd for $C_{50}H_{50}O_{16}P_4Rh_2$: C, 61.86; H, 4.62; P, 7.09. Found: C, 60.32; H, 4.54; P, 6.99. IR(KBr): 1586, 1573, 1469, 1460, 1361, 1263, 1192, 1164, 1071, 1024, 936, 890, 760, 690, 603, 500 cm^{-1} . 1H NMR (C_6D_6): 7.50 (d, 24, o-aromatic (phosphite)), 7.03 (dd, 24, m-aromatic (phosphite)), 6.86 (t, 12, p-aromatic (phosphite)), 6.75 (s, 4, aromatic), 3.21 (s, 4, benzyl), 1.53 (s, 12, methyl).

[p-Xyl]enebis(3-(2,4-pentanedionato))bis(rhodium bis(triphenyl phosphine)) (5).

To complex **1** (0.032g, 0.025mmol) in degassed THF (5mL) under nitrogen is added triphenyl phosphine (0.10g, 0.362mmol) in THF (1mL). The reaction mixture is stirred at room temperature for 2 h, the solvent removed in vacuo, and diethyl ether (5 mL) is added. The solids are filtered, washed with diethyl ether (25 mL), and dried in vacuo. Yield, 0.041g (91%). Anal. Calcd for $C_{50}H_{50}O_4P_4Rh_2$: C, 69.49; H, 5.19; P, 7.96. Found: C, 69.80; H, 4.97; P, 8.08. IR(KBr): 1557, 1463, 1436, 1363, 1280, 1190, 1123, 1098, 755, 727, 701, 543 cm^{-1} . 1H NMR (C_6D_6):

7.85 (m, 24, aromatic), 6.93 (m, 40, aromatic), 3.50 (s, 4, benzyl), 1.53 (s, 12, methyl).

[p-Xyl]enebis(3-(2,4-pentanedionato))bis(rhodium(carbonyl)(triphenylphosphine)) (6).

Triethyl phosphine (5.6 μ L, 0.038 mmol) and CD_2Cl_2 (0.5mL) are distilled in vacuo into a 5m NMR tube containing **2** (0.0117g, 0.019 mmol), and the tube is sealed in vacuo. The reaction product is identified by 1H NMR spectroscopy only. 1H NMR (CD_2Cl_2): 7.04 (s, 4, aromatic), 3.67 (s, 4, benzyl), 2.07 (s, 6, methyl), 1.92 (s, 6, methyl), 1.82 (dq, 12, $P(CH_2CH_3)_3$, $J_{PH}=7.6$), 1.19 (dt, 18, $P(CH_2CH_3)_3$, $J_{PH}=16.6$ Hz).

[p-Xyl]enebis(3-(2,4-pentanedionato))bis(rhodium carbonyl)-bis(diphenylphosphino)propane (Z).

Bis(diphenylphosphino)propane (0.233g, 0.57mmol) in THF (50mL) is added over a 30 minute period to a THF solution (50mL) of **2** (0.350g, 0.57 mmol) under N_2 . The reaction mixture is stirred an additional 45 minutes and the solvent volume reduced to 50 mL in vacuo. Degassed diethyl ether (50 mL) is added and the yellow precipitate is filtered, washed with ether and dried in vacuo. Yield, 0.45g (81%). Anal. Calcd for $C_{67}H_{46}P_2O_6Rh_2$: C, 57.91; H, 4.77; P, 6.35. Found: C, 57.60; H, 4.69; P, 5.93. IR (nujol): 1965, 1562, 1436, 1280, 1164, 1101, 1020, 950, 746, 700 cm^{-1} . 1H NMR (C_6D_6): 7.71 (m, 8, ortho- PPH_2), 7.02 (m, 12, meta-, para- PPH_2), 6.82 (s, 4, aromatic), 3.41 (s, 4, benzyl), 2.64 (dt, 4, $CH_2(CH_2PPH_2)_2$), 2.17 (m, 2, $CH_2(CH_2PPH_2)_2$), 2.03 (s, 6, methyl), 1.62 (s, 6, methyl). ^{31}P (H) (30% C_6D_6/C_6H_6): 43.78 (d, $J_{HP}=172.7$ Hz). MW, Calcd for: x=1, 975g/mole; x=2, 1950g/mole. Found (THF): 1552g/mole. (Determined by vapor pressure osmometry, Galbraith Laboratories.)

Molecular-exclusion chromatography. Bio-Beads SX4 were placed in CH_2Cl_2 and packed into a 50 mL buret using CH_2Cl_2 as the eluant yielding a $13'' \times 1/2''$ column. Six rhodium and iridium complexes were then used to obtain a calibration curve for molecular weight. The complexes (10 mg) were dissolved in 0.5 mL of CH_2Cl_2 , loaded onto the column and eluted with CH_2Cl_2 . The time for elution for

each complex was measured and plotted against log (molecular weight) as shown in Figure 1. Complex **2** was then treated in a similar fashion. Band 7.1 is given with complex **2** formulated as a monomer (M_n=975g/mol) while band 7.2 is given with a dimer formulation (M_n=1950g/mol). The complexes used as standards, their molecular weights, and retention times are given in Table I.

Hydrogenation of C₃H₆ using (Mn(P(OPh)₃)₂)₂VI(acac)₂ (**Δ**). A 500 mL flask containing complex **Δ** (12.9g, 7.4x10⁻³ mmol) in toluene (10 mL) is charged with propylene (92 torr) and H₂ (228 torr). The reaction mixture is stirred at room temperature (20°C) and the gas phase is examined periodically by gas chromatography using a 12m x 1/4" Poropak Q on Chromosorb P column.

[P-Xyllylenebis(3-(2,4-pentanedionato))][bis(1-iridium(cyclooctadiene))] (**8**).

[Ir(μ-Cl)(1,5-COO)]₂ (0.60g, 0.80mmol) and P-Xyllylenebis(3-(2,4-pentanedionato)) (0.27 g, 0.80 mmol) are combined under H₂ in degassed diethyl ether (10mL) and aqueous KOH (2.5mL, 1M) is then added. The solution is stirred for 30 min, water is added (20 mL) and the ether is removed in vacuo. The yellow solid is filtered in air, washed with isopropanol (20 mL), pentane (20 mL) and diethyl ether (10 mL) and dried in vacuo. Yield, 0.58g (72%). Anal. Calcd for C₃₄H₄₄O₄Ir₂: C, 45.31; H, 4.93; O, 7.10. Found: C, 44.90; H, 5.02; O, 7.17. IR(KBr): 1545, 1446, 1347, 1280, 1160, 1005, 980, 954, 914, 756, 639, 464 cm⁻¹. ¹H NMR (CD₂Cl₂): 7.04 (s, 4, aromatic), 3.91 (s, 8, vinyl), 3.72 (s, 4, benzylic), 2.21, 1.64 (m, 16, methylene), 2.03 (s, 12, methyl).

[P-Xyllylenebis(3-(2,4-pentanedionato))][bis(1-iridium di(carbonyl))] (**9**).

CO gas is passed through a stirred suspension of **8** (0.126g, 0.14 mmol) in hexane (20 mL) for 30 min. The purple solid is filtered, washed with diethyl ether (25 mL) and dried in vacuo. Yield, 0.11 g (99%). Anal. Calcd for C₂₂H₂₀O₈Ir₂: C, 33.16; H, 2.53; O, 16.06. Found: C, 32.65; H, 2.52; O, 16.11. IR(KBr): 2051, 1965, 1554, 1455, 1335, 1291, 1170, 955. ¹H NMR (C₆D₆): 6.67 (s, 4, aromatic), 3.17 (s, 4, benzylic), 1.66 (s, 12, methyl). UV-Vis (C₆H₆): λ_{max} nm (ε): 375 (2400),

330(12,500), 310(15,400).

[P-Xyllylenebis(3-(2,4-pentanedionato))][bis(1-iridium(carbonyl))(triphenylphosphine))] (**10**).

Triphenylphosphine (0.026g, 0.10 mmol) in THF (10 mL) is added to **9** (0.040g, 0.05mmol) under nitrogen and the mixture stirred at room temperature for 1 h. Degassed pentane (20 mL) is added and the yellow precipitate filtered and washed with diethylether (10 mL). Yield, 0.055g (87%). Anal. Calcd for C₅₆H₅₀P₂O₆Ir₂: C, 53.15; H, 3.99; P, 4.89. Found: C, 54.00; H, 4.08; P, 5.20. IR(KBr): 1950, 1554, 1455, 1433, 1350, 1287, 1099, 750, 696, 546cm⁻¹. ¹H NMR (C₆D₆): 7.87 (m, 12, aromatic), 7.01 (m, 18, aromatic), 6.76 (s, 4, aromatic), 3.34 (s, 4, benzylic), 1.87 (s, 6, methyl), 1.41 (s, 6, methyl).

[P-Xyllylenebis(3-(2,4-pentanedionato))][bis(1-iridium bis(triphenylphosphine))] (**11**).

To **9** (0.15g, 0.17 mmol) under nitrogen is added triphenylphosphine (0.175g, 0.67 mmol) dissolved in degassed THF (10 mL). The reaction mixture is refluxed for 4 h and then treated with degassed hexanes (10 mL). The solution is cooled to room temperature, filtered under nitrogen, and washed with diethyl ether (5mL). Yield, 0.27g (92%). Anal. Calcd for C₉₀H₈₀O₄P₄Ir₂: C, 62.34; H, 4.66; P, 7.14. Found: C, 61.96; H, 4.54; P, 7.10. IR (KBr): 1551, 1432, 1362, 1284, 1092, 746, 695, 564, 533cm⁻¹. ¹H NMR(C₆D₆): 7.88 (m, 24, aromatic), 6.93 (m, 36, aromatic), 6.79 (s, 4, aromatic), 3.44 (s, 4, benzylic), 1.32 (s, 12, methyl).

[P-Xyllylenebis(3-(2,4-pentanedionato))][bis(1-iridium(σ-allyl))(carbonyl)] (triphenylphosphine)(bromide)] (**12**).

Triphenylphosphine (0.037g, 0.14 mmol) in THF (6 mL) is added to **9** (0.056g, 0.07 mmol) under H₂ and the solution is refluxed for 10 min. Allyl bromide (12 μL, 0.14mmol) is then added and the reaction mixture refluxed for 12 h. The solution is cooled to room temperature and degassed hexane (10 mL) is then added. The tan solid is filtered washed with hexanes (10 mL) and dried in vacuo. Yield, 0.09g (93%) Anal. Calcd for C₆₂H₆₀O₆P₂Br₂Ir₂: C, 49.40; H, 3.98. Found: C, 49.81; H, 4.10. IR(KBr): 2038, 1568, 1453, 1435, 1316, 1283, 1099, 750, 698, 546,

520 cm^{-1} . ^1H NMR (C_6D_6): 7.90 (m, 12, aromatic), 6.9-7.1 (m, 22, aromatic), 6.17 (m, 2, vinyl), 4.94 (m, 4, vinyl), 3.41 (s, 4, benzy), 2.91 (m, 2, Ir-CH_2), 2.80 (m, 2, Ir-CH_2), 1.94 (s, 6, methyl), 1.65 (s, 6, methyl).

$[\text{Ir}(\text{triphenylphosphine})_2(\text{3-(2,6-pentadienylidene)-1,5-naphthoquinone)}]\text{bromide}$ (13).

Triphenylphosphine (0.6079g, 0.26mmol) and **2** (0.103g, 0.13mmol) are combined in THF (20 mL) under H_2 . Benzylbromide (31 μL , 0.26mmol) is added to the reaction solution which is then refluxed 3 h. The solvent is removed in vacuo, diethyl ether (10 mL) is added, and the tan solid is filtered and dried in vacuo. The complex is characterized by IR and ^1H NMR spectroscopy. IR(KBr): 2034, 1569, 1451, 1436, 1360, 1282, 1095, 750, 698, 547, 532 cm^{-1} . ^1H NMR (C_6D_6): 7.94 (m, 12, o-aromatic PPh_3), 6.9-7.4 (multiplets, remaining aromatics + C_6H_6), 3.48 (dd, 2, Ir-CH_2), 3.39 (s, 4, benzylic), 2.96 (dd, 2, Ir-CH_2), 1.64 (s, 6, CH_3), 1.63 (s, 6, CH_3).

$\text{Iridium}(\text{1,5-COO})(\text{acac})$ (14). This complex was not prepared by the literature method¹² but by a modification of the procedure used to prepare **2**, using acetylacetone in place of $\text{xy}(\text{acac})_2$. Yield, 81%. The complex gave satisfactory IR and ^1H NMR spectra.

$\text{Iridium}(\text{CO})_2(\text{acac})$ (15). Similarly, this complex was not prepared by the literature method¹³ but by passing CO through a hexane suspension of $\text{Ir}(\text{COO})(\text{acac})$. Yield, 94%. UV-Vis (C_6H_6): λ_{max} (m(c)), 375 sh(560), 338(2550), 300(5140). The complex gave satisfactory IR and ^1H NMR spectra.

$\text{Iridium}(\text{PPh}_3)_2(\text{acac})$ (16). Triphenylphosphine (0.283g, 1.08mmol) dissolved in THF (10mL) is added to $\text{Ir}(\text{COO})(\text{acac})$ (0.214g, 0.536 mmol) under nitrogen. The solution is refluxed 3 hours, cooled to room temperature, treated with hexanes (30 mL) and allowed to stand overnight. The resulting yellow crystals are then filtered and washed with diethyl ether (5 mL). Yield 0.39 g (90%). Anal. Calcd for $\text{C}_{41}\text{H}_{37}\text{O}_2\text{P}_2\text{Ir}$: C, 60.36; H, 4.58; P, 7.59. Found: C, 60.51; H, 4.41; P,

7.43. IR(KBr): 1561, 1516, 1476, 1431, 1392, 1273, 1182, 1092, 1027, 735, 698, 564, 528 cm^{-1} . ^1H NMR (C_6D_6): 7.84 (m, 12, aromatic) 6.92 (m, 18, aromatic), 5.31 (s, 1, central-CH, acac), 1.29 (s, 6, methyl)

$\text{Iridium}(\text{o-allyl})(\text{carbonyl})(\text{acac})(\text{triphenylphosphine})(\text{bromide})$ (17).

Triphenylphosphine (0.0153g, 0.0504mmol) in degassed benzene (10 mL) is added to $\text{Ir}(\text{CO})_2(\text{acac})$ under nitrogen, and the resulting solution is refluxed for 10 minutes. The mixture is cooled to room temperature, treated with allyl bromide (10 μL , 0.116mmol) and stirred for 18 hours. The solvent is removed in vacuo, and the solid is recrystallized from acetone/iso-propanol. The complex is identified by IR and ^1H NMR spectroscopy. IR(mujol): 2040, 1568, 1520, 1433, 1288, 1190, 1096, 752, 696 cm^{-1} . ^1H NMR (C_6D_6): 7.90 (m, 6, aromatic), 7.0 (m, 9, aromatic), 6.1 (m, 1, =CH-CH₂), 5.2 (s, 1, HC(COCH₃)₂), 4.9 (m, 2, =CH₂), 2.85 (ddd, 1, CH-Ir), 2.45 (dd, 1, CH⁺-Ir), 1.80 (s, 3, methyl), 1.50 (s, 3, methyl).

Reaction of $\text{Ir}(\text{PPh}_3)_2(\text{acac})$ with H_2 . d_6 -benzene (0.5 mL) is distilled in vacuo into a 5 mm ^1H NMR tube containing complex **16** (2mg). The tube is sealed under H_2 (440 torr) and heated to 70°C. The reaction is monitored periodically by ^1H NMR spectroscopy. The hydrogenation is shown to be complete after two days by comparison of its ^1H NMR spectrum with literature values.

^1H NMR (C_6D_6): 7.99 (m, 12, ortho-aromatic), 7.05 (m, 18, meta-,para-aromatic), 4.65 (s, 1, methine), 1.34 (s, 6, methyl), δ 24.75 (t, 2, Ir-H).

Reaction of $\text{Ir}(\text{COO})(\text{acac})$ with H_2 and PPh_3 . C_6D_6 (0.5 mL) is distilled in vacuo into a 5 mm ^1H NMR tube containing $\text{Ir}(\text{COO})(\text{acac})$ (2.2 mg, 5.5 μmol) and PPh_3 (3.2mg,12 μmol) and the tube is sealed under H_2 (600 torr). The reaction is monitored by ^1H NMR spectroscopy (see Results and Discussion section for more detailed analysis).

Reaction of $[p\text{-xylylenabis(3-(2,4-pentanedionato))bis(1r(cdo))}]$ with PPh_3 and H_2 . Hydrogen is passed through an acetone solution (10 mL) of **2** (0.053g, 0.059 mmol) and PPh_3 (0.062g, 0.236 mmol) for 10 min. The tan precipitate is filtered, washed with pentane (10 mL) and dried *in vacuo*, yielding a mixture of iridium hydride complexes. $\text{fac-IrH}_3(\text{PPh}_3)_3$ selectively crystallizes from a $\text{d}_6\text{-Me}_2\text{SO}$ solution of the tan solid as white needles. $^1\text{H NMR}(\text{C}_6\text{D}_6)$: 7.39 ppm (m, 18, o- PPh_3), 6.81 ppm (m, 27, m-, p- PPh_3), -11.45 ppm (s, 3, IrH). (see Results and Discussion for more detailed analysis).

Results and Discussion

As we anticipated at the outset of this study, the $\text{xy}(\text{acac})_2^{2-}$ ligand readily forms binuclear Rh and Ir complexes for which the mononuclear $\text{mono}(\text{acac})$ analogues are known. The method of preparation involves substitution of the mononuclear acac moieties of **1** for chloride in the $\mu\text{-Cl}$ dimers of $\text{Rh}(\text{I})$ and $\text{Ir}(\text{I})$, followed by substitution reactions of the remaining neutral ligands. The results obtained including subsequent reaction chemistry of the $\text{Rh}(\text{I})$ and $\text{Ir}(\text{I})$ binuclear complexes of $\text{xy}(\text{acac})_2$ are now discussed in detail.

Rhodium Complexes. The dimer $[\text{Rh}(\mu\text{-Cl})(1.5\text{-CDO})]_2$ reacts with **1** and 2 equiv of base to produce the binuclear $\text{Rh}(\text{I})$ cyclooctadiene complex, **1**, which is isolated as an air stable yellow solid. Its IR spectrum shows a strong band at 1560 cm^{-1} assignable to a bidentate β -diketonate group. The absence of bands near 1700 cm^{-1} indicates both β -diketonate moieties are coordinated to metal centers producing a binuclear complex. The mass spectrum of **1** exhibits the molecular ion (M^+) at 722 m/e. Other fragments observed include the $[M^+ - (\text{C}_2\text{H}_3\text{O})]$ ion and a base peak attributable to $[M^+ - (\text{C}_2\text{H}_3) - (\text{Rh}(1.5\text{-CDO}))]$. The 400-MHz $^1\text{H NMR}$ spectrum of **1** further confirms its binuclear structure (see Table I). A singlet due to the equivalent aromatic protons of the binucleating ligand appears at 7.03 ppm while the benzylic and methyl protons appear as singlets at 3.60 and 1.96 ppm, respectively. The coordinated cyclooctadiene has resonances at 4.05, 2.41 and 1.85 ppm which can be assigned to the vinyl protons and the non-equivalent methylene protons.

The chelating diolefin ligand, 1,5-CDO, is easily displaced by either CO or PPh_3 . Thus the reaction of **1** with CO in a hexane suspension results in the isolation of the orange air-stable rhodium carbonyl complex, **2**. Its IR spectrum contains two strong bands at 2070 and 1970 cm^{-1} , assignable to the symmetric and anti-symmetric stretches of the *cis* carbonyl ligands. A strong band at 1560 cm^{-1} shows that the β -diketonate has remained chelated to the rhodium center. The loss of cyclooctadiene is confirmed by the $^1\text{H NMR}$ spectrum of **2**, which consists of three singlets at 7.01, 3.70 and 2.09 ppm assignable to the aromatic, benzylic and

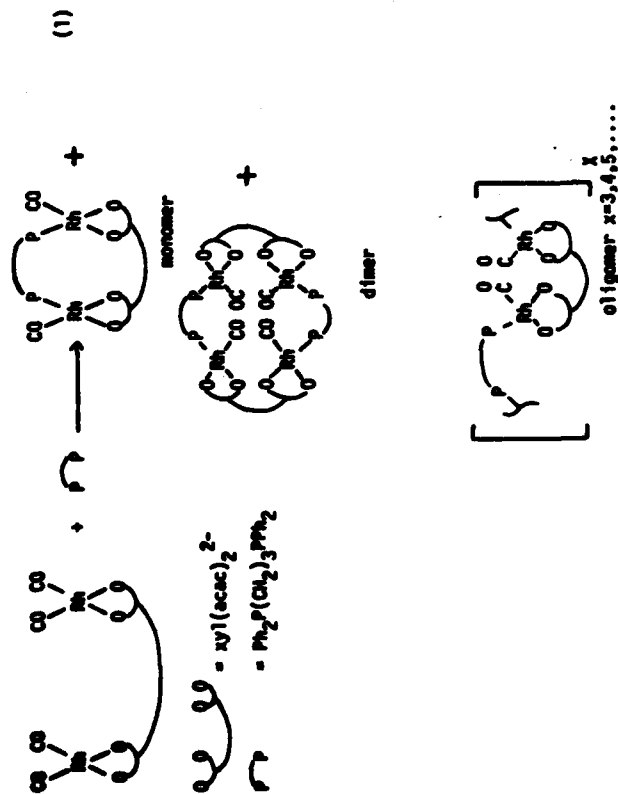
Since the reaction of the dicarbonyl complex, **2**, with phosphines results in the displacement of a single CO ligand from each rhodium center, we envisioned the addition of a second bridging moiety between the metal centers via the reaction of **2** with bis(phosphine) ligands. Thus, the reaction of bis(diphenylphosphine)propane with $[\text{Rh}(\text{CO})_2\text{Xyl}(\text{acac})_2]$ in THF occurs as expected resulting in the formation of the rhodium'(phosphine)(carbonyl) complex, **3**. The IR spectrum of complex **3** contains a single band in the 1900-2100 cm^{-1} region indicating the presence of a single carbonyl ligand on each metal center. The β -diketonate ligand remains bound in a bidentate fashion as shown by the absence of bands near 1700 cm^{-1} . Not surprisingly the bis(phosphine) ligand are coordinated to equivalent ν centers as indicated by the presence of a doublet ($J=172.7\text{ Hz}$) at 43.78 ppm in the ^{31}P (^1H) NMR spectrum of **3**. No free phosphine is detected by ^{31}P NMR spect. ν . The mononuclear rhodium complex, $\text{Rh}(\text{CO})(\text{PPh}_3)_3(\text{acac})$ exhibits a resonance at 48.7 ppm (CHCl_3 solution, $J_{\text{Rh-P}}=175.4\text{ Hz}$) in its ^{31}P NMR spectrum.³ The elemental analysis and ^1H NMR spectrum of complex **3** are consistent with the reaction of one equivalent of bis (phosphine) ligand with one equivalent of binuclear rhodium complex, **2**. The ^1H NMR spectrum of **3** contains resonances in the aromatic region due to the phenyl groups of the phosphine ligand and due to the phenylene group of the bis (β -diketonate) moiety. The inequivalent methyl groups of $\text{Xyl}(\text{acac})_2$ yield resonances at 2.03 and 1.62 ppm, while the benzylic protons appear at 3.41 ppm, similar to the corresponding resonances observed for $[\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Xyl}(\text{acac})_2]$. The propylene bridge of the bis(phosphine) ligand gives rise to two multiplets. The methylene hydrogens adjacent to phosphorus appear at 2.64 ppm while the central methylene hydrogens produce a multiplet at 2.17 ppm.

Several products are possible in this reaction, as shown in Equation (1). They

methyl protons, respectively, of the $\text{Xyl}(\text{acac})_2$ ligand. Refluxing benzene solutions of complex **2** show no reaction with either H_2 or CH_3I but complex **2** does react with HCl causing the protonation and loss of the bridging ligand, and the formation of $[\text{Rh}(\mu\text{-Cl})(\text{CO})_2]_2$. The same ligand displacement is observed for the mononuclear complex $\text{Rh}(\text{CO})(\text{PPh}_3)_3(\text{acac})$.¹⁴

The reaction of the binuclear rhodium cyclooctadiene complex, **1**, with triphenyl phosphine results in the displacement of the diolefin ligand and the formation of the bis phosphine complex, **5**. This complex is slightly air sensitive, gradually decomposing over several hours in solution. Its IR spectrum verifies the presence of the chelated β -diketonate ($\nu_{\text{acac}}=1557\text{ cm}^{-1}$), and its ^1H NMR spectrum shows the loss of cyclooctadiene resonances and the coordination of triphenyl phosphine. The aromatic region contains resonances due to coordinated PPh_3 and the aromatic hydrogens from the bridging $\text{Xyl}(\text{acac})_2$ ligand. The benzylic protons appear as a singlet at 3.5 ppm and methyl protons are present at 1.53 ppm also as a singlet.

Displacement of CO. The dicarbonyl complex **2** reacts readily with excess triphenylphosphine, causing the displacement of one CO from each metal center and yielding the mixed phosphine carbonyl complex, **3**. A similar reaction occurs with $\text{Rh}(\text{CO})_2(\text{acac})$.⁷ The IR spectrum of **3** contains one carbonyl stretch at 1950 cm^{-1} , indicating the loss of only one carbonyl from each rhodium center. A band at 1550 cm^{-1} confirms the presence of the chelated β -diketonate group. The ^1H NMR spectrum of **3** shows the presence of one coordinated PPh_3 per metal center and contains a singlet at 7.00 ppm assignable to the aromatic protons on the bridging ligand. The methyl groups are no longer equivalent due to the loss of symmetry at the $\text{Rh}(\text{I})$ center, and appear as singlets at 2.10 and 1.62 ppm. The benzylic protons are not affected by this loss of symmetry and remain as a singlet at 3.62 ppm. The rhodium dicarbonyl complex, **2**, also reacts with triethylphosphine to produce the carbonyl phosphine complex, **6**, as identified by its ^1H spectrum.



range from a 1:1 monomer which contains an intramolecularly bridging bis(phosphine) ligand, to oligomers which contain intermolecular phosphine bridges. Entropy favors the formation of the intramolecularly bridged monomer as long as the binucleating $\text{xy}(\text{acac})_2^{2-}$ framework is flexible enough to allow a face-to-face approach of the rhodium centers. Molecular weight measurement of complex Z in THF yields an average molecular weight of 1552. This value is intermediate between a monomer (M_n=975) and a dimer (M_n=1950) and indicates that a portion of complex Z is monomeric. Analysis of this reaction product by molecular-exclusion chromatography gives results as shown in Figure 1 and Table II. By comparing the relative retention times of known molecular weight standards with that of complex Z it is apparent that some monomer is present in the complex mixture. The broadness of the band indicates that some dimer is present also. These results suggest that there exists enough conformational flexibility in the $\text{xy}(\text{acac})_2$ framework to allow

a face-to-face approach of the metal centers which may then be locked by the binding of a bridging bis(phosphine) ligand. Attempts to isolate in crystalline form a pure sample of the monomeric intramolecularly bridged bis(phosphine) species are now in progress.

While the reaction of the rhodium dicarbonyl complex, **2**, with phosphines leads to a mixed carbonyl, phosphine complex, the reaction of **2** with triphenylphosphite results in complete displacement of the CO ligands yielding the binuclear bis phosphite complex **4**. This reaction parallels that demonstrated for the mononuclear complex, $\text{Rh}(\text{CO})_2(\text{acac})$.¹⁵ The phosphite complex, **4**, prepared in 92% yield from the dicarbonyl complex, **2**, is isolated as a yellow, crystalline solid. The IR spectrum of **4** exhibits no bands in the region 1800-2200 cm^{-1} indicating complete loss of CO from the rhodium center. The β -diketonate groups remain chelated as shown by the band at 1573 cm^{-1} and the absence of bands near 1700 cm^{-1} . The ^1H NMR spectrum of **4** contains the following resonances. The aromatic protons of the phosphite ligand, $\text{P}(\text{OPh})_3$, are completely resolved and appear as multiplets at 7.50, 7.03, and 6.86 ppm assignable to the ortho-, meta-, and para-protons, respectively. A singlet at 6.75 ppm is due to the aromatic protons of the $\text{xy}(\text{acac})_2$ ligand. The benzylic hydrogens give rise to a singlet at 3.21 ppm and the equivalent methyl groups produce a singlet at 1.53 ppm. The mononuclear complex $\text{Rh}(\text{P}(\text{OPh})_3)_2(\text{acac})$ is an air-stable solid but the binuclear complex, **4**, decomposes in the solid state, gradually becoming dark brown over a period of several weeks.

The complex $\text{Rh}(\text{P}(\text{OPh})_3)_2(\text{acac})$ is reported to be a homogeneous catalyst precursor for the hydrogenation of aromatic hydrocarbons.^{8a} We, therefore, examined briefly the activity of complex **4** as a catalyst precursor in the hydrogenation of simple olefins. Preliminary work indicates that **4** promotes the hydrogenation of propylene to propane. The rate of hydrogenation at 24°C under 320 torr or $\text{H}_2 + \text{C}_3\text{H}_6$ (2.5:1) is 8 mol of propane mol^{-1} of complex **4** h^{-1} . However, the catalyst solution exhibits signs of decomposition after 24 h reaction.

Further investigations regarding the nature of the catalytically active species indicate that with both the mononuclear and binuclear complexes, $\text{Rh}(\text{P}(\text{OPh})_3)_2(\text{acac})$ and $(\text{Rh}(\text{P}(\text{OPh})_3)_2)_2\text{Xyl}(\text{acac})_2$, respectively, the integrity of the $\text{Rh}(\text{acac})$ unit is not maintained during catalysis. Thus, complex **4** serves simply as a catalyst precursor in the hydrogenation of propylene yielding mononuclear, catalytically active species. Details regarding the $\text{Rh}(\text{P}(\text{OPh})_3)_2(\text{acac})$ system will be described elsewhere.¹⁶

Iridium Complexes.

The same synthetic procedures used to make the rhodium complexes are used to prepare the iridium systems. In general, the iridium complexes are more air sensitive than their rhodium analogues. The binuclear iridium cyclooctadiene complex **9** is prepared from $\text{Xyl}(\text{acac})_2^{2-}$, generated in situ from **1** + KOH, and $[\text{Ir}(\mu\text{-Cl})(1,5\text{-COD})]_2$. This compound decomposes in air within several hours in solution but is air stable in the solid state. Its IR spectrum contains a band at 1545 cm^{-1} typical of a chelated β -diketonate. Its ^1H NMR spectrum is nearly identical to that of the binuclear rhodium complex **1**, with only minor differences in chemical shifts (see Table II).

The iridium complex undergoes the same basic reaction chemistry as its rhodium counterpart, and as its mononuclear analogue $\text{Ir}(1,5\text{-COD})(\text{acac})$, with cyclooctadiene being easily displaced by either carbon monoxide or triphenylphosphine, producing complexes **2** and **11**, respectively. The iridium carbonyl complex, **2**, is an air stable purple solid, prepared by passing CO through a hexane suspension of the COD complex **9**. Its IR spectrum exhibits two carbonyl stretches at 2051 and 1965 cm^{-1} and a β -diketonate band at 1554 cm^{-1} . Its ^1H NMR spectrum contains three singlets similar to the spectrum of complex **2**. Refluxing benzene solutions of the iridium carbonyl complex, **2**, exhibit no reaction with H_2 or CH_3I .

Displacement of CO. The iridium carbonyl complex, **2**, reacts with phosphines, resulting in the loss of only one carbonyl ligand from each metal center to give mixed carbonyl phosphine species. Thus **2** reacts with triphenylphosphine to give complex **10**, as identified by its IR and ^1H NMR spectra. The IR spectrum contains a single carbonyl stretch at 1950 cm^{-1} and a band at 1554 cm^{-1} due to the chelated β -diketonate group. While the rhodium phosphine carbonyl complex, **3**, is fairly unreactive, the analogous iridium complex, **10**, is easily oxidized in solution, and decomposes in CHCl_3 . It also undergoes oxidative addition reactions yielding iridium (III) complexes.

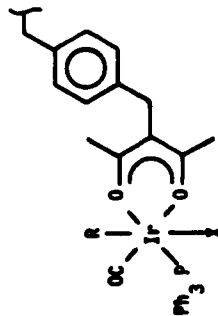
Oxidative additions. Whereas the binuclear rhodium complex, **3**, was found to be inert towards the oxidative addition of MeI or BzBr, the analogous iridium complex, **10**, easily undergoes oxidative additions. Thus, the reaction of **2** with allyl bromide results in the formation of a α -bonded allyl complex, **12**, as identified by its IR and ^1H NMR spectra. In the carbonyl region of the IR spectrum we observe one band at 2038 cm^{-1} . The shift of 88 cm^{-1} from ν_{CO} in **10** to higher frequency indicates the oxidation of the Ir(I) to Ir(III) with concomitant decrease in the back-bonding to the carbonyl ligand.¹⁷ The β -diketonate group remains chelated as indicated by a strong band at 1568 cm^{-1} and the absence of bands in the region near 1700 cm^{-1} . The $400\text{-MHz } ^1\text{H}$ NMR spectrum contains the following resonances. The α -bonded allyl gives rise to a multiplet at 5.93 ppm due to the central vinyl proton, overlapping resonances at 4.95 ppm assignable to the terminal vinyl protons and multiplets at 2.91 and 2.57 ppm assignable to nonequivalent methylene resonances for the iridium-bound $-\text{CH}_2-$ group. The α -methylene hydrogens are geminally coupled ($J_{\text{gem}} = 9.3\text{ Hz}$) and both are coupled to the vicinal vinyl hydrogen ($J_{\text{vic}} = 6.4\text{ Hz}$). The methylene resonance which appears at 2.91 ppm contains, in addition to the above couplings, a phosphorus coupling of 4.4 Hz . The observation of phosphorus coupling to only one of the methylene hydrogens suggests that the allyl group is held in a specific orientation with rotation about the metal-carbon bond restricted, possibly as a result of the

presence of the bulky phosphine ligand. A similar coupling pattern is observed for the iridium(III) benzyl complex, **12**.

The reaction of **10** with benzylbromide results in the oxidative addition of the allyl halide and the formation of the iridium(III) benzyl complex, **13**. As observed for complex **12**, the IR spectrum of **13** indicates the formation of an iridium(III) carbonyl complex by the appearance of ν_{CO} at 2034cm^{-1} . In the ^1H NMR spectrum of **13**, two multiplets are observed which are assigned to nonequivalent benzylic hydrogens. Both resonances contain geminal coupling of 9.5 Hz, in addition to phosphorus coupling.

The upfield resonance has a coupling to phosphorus of 2.4 Hz and the downfield resonance has J_{P-H} of 3.5 Hz.

The iridium(III) centers in complexes **12** and **13** are assigned octahedral coordination geometries. Based on the known trans stereochemistry of RX oxidative addition, as shown, for example, by the trans addition of MeI to $\text{Rh}(\text{PPh}_3)_2(\text{acac})$, **14** we assign the structures of **12** and **13** as **11** where $R = \alpha\text{-allyl}$, benzyl.



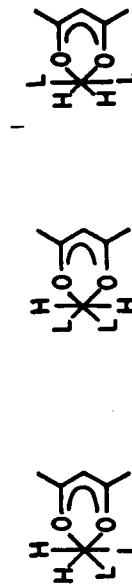
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The oxidative addition of allyl bromide to the mononuclear analogue, $\text{Ir}(\text{CO})_2(\text{PPh}_3)(\text{acac})$, was also examined. This reaction produces the iridium(III) allyl complex, **17**. Its IR spectrum shows a band at 2040cm^{-1} due to ν_{CO} and bands at 1568 and 1520cm^{-1} assignable to the chelating acac group. The ^1H NMR spectrum of **17** contains resonances due to coordinated triphenylphosphine at 7.9 and 6.96 ppm. The

acac ligand has resonances at 5.21, 1.81 and 1.52 ppm due, respectively, to the central methine proton, and the two inequivalent methyl groups. The $\alpha\text{-allyl}$ group has resonances fairly similar to the binuclear species, **12**. A multiplet appears at 6.1 ppm assignable to the central vinylic proton while the terminal vinyl protons appear at 4.9 ppm as overlapping multiplets. The downfield methylene resonance at 2.85 contains geminal coupling of 8.2 Hz, phosphine coupling of 4.2 Hz and vicinal coupling to the vinyl proton of 6.5 Hz. The upfield $\alpha\text{-methylene}$ resonance contains geminal coupling and coupling to the vinyl proton of 6.4 Hz.

Reactions with H_2 . In order to determine the potential activity of the binuclear iridium complexes, **8** - **11**, as homogeneous hydrogenation catalysts we set out to examine their reactivity with H_2 . Studies by Aréne have shown that the complex $\text{IrH}_2(\text{PPh}_3)_2(\text{acac})$ (**18**) forms via the reaction of $\text{IrH}_3(\text{PPh}_3)_2$ with H-acac . **18** As a starting point for our studies, we prepared the iridium complex, $\text{Ir}(\text{PPh}_3)_2(\text{acac})$, **16**, and examined its reaction with H_2 . The complex $\text{IrH}_2(\text{PPh}_3)_2(\text{acac})$, **18**, is formed from the reaction of **16** + H_2 as identified by its ^1H NMR spectrum and comparison with the previously reported spectrum ¹⁸ ($J_{\text{Ir-H}} = -24.7\text{ppm}$, t , $J = 17.1\text{Hz}$).

Three stereochemistries are possible for complex **18**, shown as **19**, **20** and **21**, and



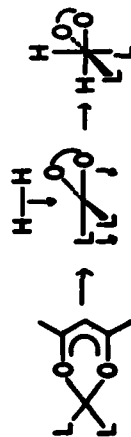
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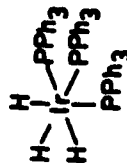
on the basis of the observed chemical shift and coupling constants for the iridium hydride, complex **18** is assigned structure **21**.

However, the initially formed H_2 addition product cannot have the stereochemistry shown as **21** if the addition is a cis concerted addition and occurs on a face of the square plane with mutually trans ligands bending out of the square plane away from the added H_2 as shown below.

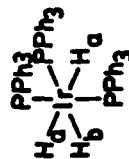


This reaction results in the formation of the isomer whose stereochemistry is shown as **III**. If the oxidative addition were to occur in this fashion, then the dihydride species **III** which initially forms rearranges to give the observed product, **V**. An alternative explanation to account for the observed product is the oxidative addition of H_2 to an iridium species other than $Ir(PPh_3)_2(acac)$, possibly via loss of phosphine prior to oxidative addition.

During the course of the reaction of **II** + H_2 , several other hydride resonances are observed in the -8 to -14 ppm region of the 1H NMR spectrum. If the iridium(I) bis phosphine complex, **II**, is prepared *in situ* from $Ir(COD)(acac) + PPh_3$ under H_2 , these hydride resonances are much more evident. Based on the observed coupling constants as determined through selective homonuclear decoupling, we identify these additional hydride resonances as belonging to the *fac*- and *mer*-isomers of the iridium(III) trihydride complex, $IrH_3(PPh_3)_3$, shown as structures **VI** and **VII**, respectively.



VI



VII

In the 1H NMR spectrum of the facial isomer, **VI**, the equivalent hydrides appear as a complex multiplet centered at -11.38 ppm, which contain a large trans-phosphorus coupling of 120 Hz and a smaller *cis* phosphorus coupling of ca. 18 Hz. The spectrum of the meridional isomer, **VII**, exhibits two complex multiplets at -10.2 and -12.1 ppm. The H_b multiplet (-12.1 ppm) contains a large trans-phosphorus coupling of 116 Hz and J_{cis-P} of 22 Hz, while proton H_a gives rise to an apparent quartet with a *cis*-phosphorus coupling of 16 Hz.¹⁹ Comparison of the hydride spectra of **VI** and **VII** with the spectra of the closely related iridium complexes $IrH_3(PET_2Ph)_3$ and $IrH_3(PET_3)_3$ ²⁰ confirms our structural assignments.

The formation of these iridium(III) trihydride complexes, **VI** and **VII**, requires the loss of the *acac* ligand from the metal center. The presence of free triphenylphosphine facilitates this displacement and increases the amount of $IrH_3(PPh_3)_3$ formed during the reaction $H_2 + Ir(COD)(acac) + PPh_3$. These same iridium hydride complexes, **VI** and **VII**, are observed during the reaction of the binuclear iridium complex, **B** with H_2 and PPh_3 . It is thus apparent that both the binucleating bis(β -diketonate) ligand, $xyI(acac)_2$, and the simple bidentate ligand, *acac*, are easily displaced by H_2 as well as by H^+ . These observations, together with our results on the activity and stability of the rhodium complexes, $Rh(P(OPh)_3)_2(acac)_2$ and $(Rh(P(OPh)_3)_2)xyI(acac)_2$, indicate that a binuclear framework using $xyI(acac)_2$ complexes of Rh and Ir will not be maintained during simple catalytic reactions such as olefin hydrogenation and hydroformylation.

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References

1. Melnikova, R. G.; Bohra, R.; Gaur, D. P. "Metal β -Diketones and Allied Derivatives"; Academic Press: New York, 1978.
2. Gredson, D. P. Coord. Chem. Rev. 1982, **4**, 1.
3. Collman, J. P. Angew. Chem. 1965, **77**, 154.
4. Martin, D. F.; Fernelius, W. C.; Shamma, M. J. Am. Chem. Soc. 1952, **81**, 130.
5. Korshak, V. V.; Krongauz, E. S.; Berlin, A. M. J. Polymer Sci. (A) 1965, **3**, 2425.
6. Korshak, V. V.; Krongauz, E. S.; Sheina, V. E. Vysokom. Soedin. 1960, **2**, 662.
7. Bonati, F.; Wilkinson, G., J. Chem. Soc. 1964, 3156.
8. a) Pieta, D.; Trzeciak, A. M.; Ziolkowski, J. J. J. Mol. Cat. 1983, **18**, 193.
b) Shebalova, A. D.; Bystrenina, V. I.; Kravtsova, V. N.; Khidkei, M. L. Izv. Akad. Nauk. SSSR, Ser. Khim. 1975, 2101.
9. a) King, R. B.; King, A. D. Jr.; Iqbal, M. Z. J. Am. Chem. Soc. 1972, **101**, 4893.
b) Hartley, F. R.; Murray, S. G.; Nicholson, P. M. J. Mol. Cat. 1982, **16**, 363.
10. Chatt, J.; Venanzi, L. M. J. Chem. Soc. 1957, 4735.
11. Herde, J. L.; Lambert, J. C.; Senott, C. V. Inorg. Syn. 1974, **XV**, Parrshall, G. Ed., 18.
12. Robinson, S. D.; Shaw, B. L. Int. Lett. 1964, 1301.
13. Donati, F.; Upo, R. J. Organomet. Chem. 1968, **11**, 341.
14. Barlen, D. M.; Hecher, M. J.; Kamitt, R. D. W. J. Organomet. Chem. 1972, **43**, 425.
15. Trzeciak, A. M.; Ziolkowski, J. J. Inorg. Chim. Acta Lett. 1982, **64**, L267.
16. Whitmore, B. C.; Eisenberg, R. J. Am. Chem. Soc., in press.
17. Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry," 3rd ed.; Interscience: New York, 1972; p. 687.
18. Arneso, A. Gazz. Chim. Ital. 1965, **95**, 1431.

19. Irradiation of the resonance due to H_b results in the complete disappearance of the resonance due to H_a . This suggests that the hydride ligands in $mer-IrH_3(PPh_3)_3$ interconvert at room temperature. Based on the frequency separation between the two resonances of 720Hz, the rate of exchange must be slower than 1.4×10^{-3} sec but this interconversion must be faster than the rate of relaxation (T_1) of the hydride ligands in order to cause the saturation of both H_a and H_b during the decoupling experiment.

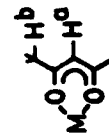
20. Mann, B. E.; Masters, C.; Shaw, B. L. J. Inorg. Nucl. Chem. 1971, **33**, 2195.

Table II. ^1H NMR Spectral Data for Binuclear and Mononuclear Complexes.

Complex	H^a	H^b	H^c	Others
1	7.03	3.60	1.96	(COO) 4.06-vinyl; 2.41, 1.85-methylene
2	7.01	3.70	2.09	
3	7.00	3.62	2.10, 1.62	(PPh ₃) 7.80-ortho; 7.30-meta, para
4	6.75	3.21	1.53	(P(OPh) ₃) 7.50-ortho; 7.03-meta; 6.85-para
5	6.93	3.50	1.53	(PPh ₃) 7.85-ortho; 6.93-meta, para
6	7.04	3.67	2.07, 1.92	(PEt ₃) 1.82-methylene; 1.19-methyl
7	6.82	3.41	2.03, 1.62	(BPPF) 7.71-ortho; 7.02-meta, para; 2.64-(CH ₂ -P); 2.17-(CH ₂ -CH ₂ -P)
8	7.04	3.72	2.03	(COO) 3.91-vinyl; 2.21, 1.64-methylene
9	6.67	3.17	1.66	
10	6.76	3.34	1.87, 1.41	(PPh ₃) 7.87-ortho; 7.01-meta, para
11	6.79	3.44	1.32	(PPh ₃) 7.88-ortho; 6.93-meta, para
12	7.0	3.41	1.94, 1.65	(allyl) 6.17-central vinyl; 4.94-terminal vinyl; 2.91, 2.58-methylene
13	6.9-7.4	3.39	1.64, 1.63	(PPh ₃) 7.90-ortho; 6.9-7.1-meta, para
				(CH ₂ Ph) 6.9-7.4-aromatics; 3.46, 2.96-methylene
				(PPh ₃) 7.94-ortho, 6.9-7.4-meta, para

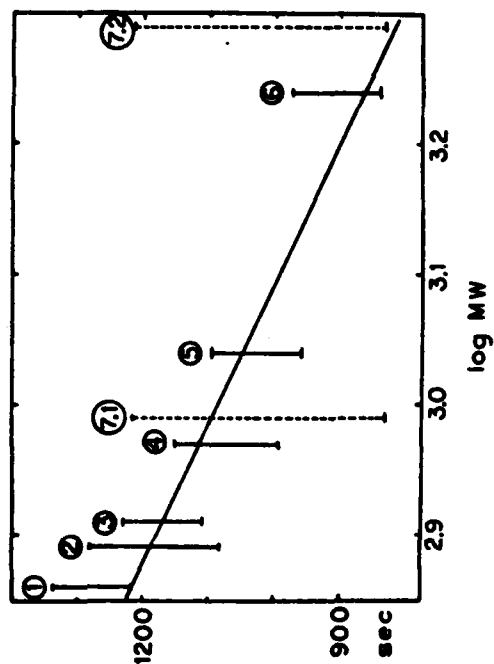
Table I. Molecular-Exclusion Chromatography data.

Complex	Molecular Weight (M)	Log(M)	Elution time (sec)
(1) [Rh(COO) ₂ xy](acac) ₂	722	2.86	1215-1335
(2) IrCl(CO)(PPh ₃) ₂	779	2.89	1080-1280
(3) Rh(P(OPh) ₃) ₂ (acac)	822	2.91	1110-1230
(4) RhCl(PPh ₃) ₃	924	2.97	990-1150
(5) Rh ₂ Cl ₂ (CO) ₂ (dpm) ₂	1101	3.04	960-1095
(6) [Rh(P(OPh) ₃) ₂ xy](acac) ₂	1746	3.24	835-975



Complex	H^a	H^b	Others
14	5.12	1.70	(COO) 4.31-vinyl; 2.21, 1.54-methylene
15	5.06	1.52	
16	5.31	1.29	(PPh ₃) 7.84-ortho; 6.92-meta, para
17	5.20	1.80, 1.50	(allyl) 6.1-central vinyl; 4.9-terminal vinyls; 2.85, 2.45-methylene

Figure 1. Plot of $\log(MW)$ vs. elution time for a series of known complexes and for complex Z.



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